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Vibrational assignments of trimethoxy benzenes

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The vibrational spectra of 1, 3, 5, —, 1, 2, 3 - and 1, 2, 4 trimethoxy benzene have not been studied earlier. The laser excited Raman spectra and the infrared absorption spectra of the compounds were recorded. Vibrational assignments of the observed frequencies are discussed in this paper.

The three trimethoxy benzene compounds from original packings (Purum grade) of Fluka (Switzerland) were used without further purification. The 4880 Å line from an Argon ion laser source (Control Laser model 901) was used as the exciting radiation and the Raman spectra were recorded with a Carl Zeiss monochromator (SPM 2) used in conjunction with a photo-multiplier tube as detector and a pen recorder Capillary cell was used in the case of 1, 2, 4 — trimethoxy benzene, which is a liquid at room temperature. The Raman spectra of the solid samples of 1, 3, 5 - and 1, 2, 3 — trimethoxy benzene were recorded at their melting points, using a special cell designed in this laboratory. The infrared spectra were recorded with a Perkin Elmer model 21 spectrophotometer.

RESULTS AND DISCUSSIONS

1, 3, 5 -trimethoxy benzene

Treating the substituent OCH_3 group as a single mass X, the 1, 3, 5- $C_6H_3X_3$ molecule may be assumed to have the symmetry D_{3h} and the thirty phenyl ring vibrations can be divided into

$$4a_1' (R,p) + 3a_2' + 7e' (i.r; R, dp) + 3a''_2 (i.r) + 3e'' (R, dp)$$

Comparative study of assignments of normal vibrations of other 1, 3, 5- $C_6H_3X_3$ molecules (Green *et al* 1971a) and the polarisation of Raman lines help identifying the observed a'_1 vibrations of 1, 3, 5- trimethoxy benzene.

The strong infrared band at 3005cm^{-1} has been assigned to ν_8 belonging to e′ class. All the e′ vibrations are expectedly strongly infrared active. The assignments of $\nu_3(a'_1)$ and $\nu_{12}(e')$ are in fact based on the intensities of the bands in the infrared and the Raman spectra.

Of the out of plane modes, ν_{15} and ν_{16} derivable according to Pitzer and Scott (1943) from b_{2g} modes 5 and 4 of benzene are assigned to the strong infrared bands at 805cm^{-1} and 722cm^{-1} respectively. The weak Raman line

at 133cm^{-1} is associated with $\nu_{17}(a_2'')$ which should be ordinarily inactive. Its appearence may mean that the assumption of D_{3h} symmetry, though valid within reasonable limits, is an approximation and this mode appears weakly in the Raman spectrum under excitation with the strong laser source.

In quite a few 1, 3, 5 symmetric trisubstituted benzene molecules the e'' ν_{19} was reported to have frequency lying in the range 500-580cm^{-1} (Green *et al* 1971a, Varsanyi, 1969) and on this basis the 498cm^{-1} Raman line has been associated with this vibrational mode.

1, 2, 3—trimethoxy benzene

Taking the molecular symmetry as C_{2v}, the thirty phenyl ring vibrations of this molecule are

$$11a_1 \text{ (i.r; R, p)} + 10b_2 \text{ (i.r; R, dp)} + 3a_2 \text{ (R, dp)} + 6b_1 \text{ (i.r ; R, dp)}.$$

The degeneracy of the e_{1u} mode 19 of benzene is removed with lowering of symmetry in the case of 1, 2, 3—$C_6H_3X_3$ molecules to C_{21v} and this mode is broken up into an a_1 and a b_2 vibration. It was pointed out by Green *et al* (1971a) that the a_1 component has a slightly greater frequency than the b_2 component. The assignment of ν_4 and ν_{28} are made accordingly. These two bands are well resolved in the infrared spectrum only.

1, 2, 4—trimethoxy benzene

The thirty phenyl ring vibrations of this molcule, which cannot have symmetry higher than C_s, are classified as

$$21a' \text{ (i. r; R, p)} + 9a'' \text{ (i. r; R, dp)}.$$

The highest C-H valence oscillation frequency 3081cm^{-1} should clearly be associated with ν_1 while the frequency 3007cm^{-1} is the obvious choice for ν_3. The two resolved strong infrared bands at 1611 and 1595cm^{-1} identify ν_4 and ν_5. In the Raman spectrum only one band with centre at about 1605cm^{-1} is observed. Doubt persists as to the assignment of the modes ν_{19}, ν_{21} and ν_{29}. Assignments of other frequencies are more or less in agreement with those reported for similar and related molecules by previous authors (Varsanyi, 1969; Green, *et al* 1971b, Marjit *et al* 1972a, b).

Internal vibrations of the substituent groups

The frequencies of vibrations associated with the stretching and bending modes of CH_3 groups are generally accepted and these assignments require no comments. Marjit *et al* (1972a, b) had assigned a frequency of about 1150cm^{-1} to CH_3 rocking and another of about 1000cm^{-1} to O-CH_3 strentching vibrations. But in accordance with the views of Varsanyi(1969) and

Table 1. Wavenumbers (cm^{-1}) of the fundamental vibrations for 1, 3, 5—trimethoxy benzene. (D_{3h} point group)

Symmetry		Wavenumber in cm^{-1} R	I.R.
a'_1	ν_1	—	—
R(p),—	ν_2	1333(m)	1333(w)
	ν_3	973(v.s.)	
	ν_4	599(m)	—
a'_2	ν_5		—
—,—	ν_6		—
	ν_7		—
e'	ν_8	—	3005(v.s)
R(dp), I.R	ν_9	1594(m)	1593(v.s.b)
	ν_{10}	1451(m)	1460(v.s.b)
	ν_{11}	1183(w.b)	1197(v.s.b)
	ν_{12}	932(w)	935(s)
	ν_{13}	408(w)	—
	ν_{14}	306(w)	—
a''_2	ν_{15}	—	805(s)
—, I.R	ν_{16}	—	722(s)
	ν_{17}	133(m)	—
e''	ν_{18}	892(w)	890(vw)
R(dp),—	ν_{19}	498(w)	—
	ν_{20}	209(m)	—

Table 2. Wavenumbers (cm^{-1}) of the fundamental vibrations for 1, 2, 3—trimethoxy benzene. (C_{2v} point group)

Symmetry		Wavenumber in cm^{-1} R	I.R
a_1	ν_1		—
R(p), I.R	ν_2	—	
	ν_3	1605(m)	—
	ν_4	1468(vw)	1479(v s)
	ν_5	1251(vw)	1246(v.s)
	ν_6	1196(m)	1179(m)
	ν_7	1109(vw)	1105(v.s.b)
	ν_8	819(vw)	815(m)
	ν_9	618(v.s)	—
	ν_{10}	413(w)	—
	ν_{11}	375(m)	—
a_2	ν_{12}	872(vw)	856(w)
R(dp),—	ν_{13}	591(v.s.sh)	—
	ν_{14}	224(v.s)	—

Table 2 (*Contd.*)

Symmetry		Wavenumber in cm^{-1} R	I.R.
b_1	ν_{15}	—	975(w)
R(dp), I.R.	ν_{16}	711(m)	727(v.s)
	ν_{17}	—	695(m)
	ν_{18}	—	—
	ν_{19}	—	—
	ν_{20}	—	—
b_2	ν_{21}	—	3002(s)
R(dp), I.R	ν_{22}	—	1588(v.s)
	ν_{23}	—	1458(v.s)
	ν_{24}	1314(w)	1288(v.s)
	ν_{25}	—	1266(m)
	ν_{26}	1173(m)	1165(s)
	ν_{27}	1093(m)	1085(v.s)
	ν_{28}	562(m.sh)	—
	ν_{29}	512(w)	—
	ν_{30}	263(v.s)	—

Table 3. Wavenumbers (cm^{-1}) of fundamental vibrations for 1, 2, 4—trimethoxy benzene. (C_s point group)

Symmetry		Wavenumber in cm^{-1} R	I.R.
a′	ν_1	3081(v.w)	—
	ν_2	—	—
R(p), I.R.	ν_3	3007(v.w)	—
	ν_4	1605(m)	1611(s)
	ν_5	1605(m)	1595(s)
	ν_6	1510(v w)	1512(v.s)
	ν_7	—	1465(v.s.b)
	ν_8	—	1299(s)
	ν_9	—	1281(v s)
	ν_{10}	1259(v.w)	1264(v.s)
	ν_{11}	—	1208(v.s)
	ν_{12}	—	1158(v.s)
	ν_{13}	1156(v.w)	1140(v.s)
	ν_{14}	—	1046(v.s)
	ν_{15}	765(v.s)	763(s)
	ν_{16}	707(w)	707(w)
	ν_{17}	551(w)	—
	ν_{18}	498(v.w)	—
	ν_{19}	377(m)	—
	ν_{20}	356(m)	—
	ν_{21}	194(s)	—

Table 3 (*Contd.*)

Symmetry		Wavenumber in cm^{-1} R	I R
a''	ν_{22}	—	931(m)
	ν_{23}	—	830(m)
R(dp), I.R.	ν_{24}	—	788(m.b)
	ν_{25}	—	695(w)
	ν_{26}	568(w)	—
	ν_{27}	464(v.w)	—
	ν_{28}	—	-
	ν_{29}	194(s)	—
	ν_{30}	—	—

Table 4. Internal vibrations of the substituent groups of 1, 3, 5—, 1, 2, 3—, & 1, 2, 4—trimethoxybenzene

Nature of Vibrations	1, 3, 5—trimethoxy benzene.		1, 2, 3—trimethoxy benzene		1, 2, 4—trimethoxy benzene.	
	R.	I.R.	R	I R.	R.	I.R
ν_{as} (CH_3)	-	2961(v.s)	-	2963(s b)	-	-
	—	2945(v.s.b)	—	2943(v s)	2938(v w)	-
ν_{s} (CH_3)	—	2908(s)	—	2908(m b)	2912(w)	-
	—	2843(v.s)		2843(v.s)	2840(w)	-
δ_{as} (CH_3)	1451(m)	1453(m)	—	1452(s)	1447(v w)	1445(v.s.b
			1430(v w)	1435(s)	1432(m)	1428(s sh)
δ_{s} (CH_3)	—	1413(v.s)	—	1422(v s)	1335(w)	-
	—	1313(m)	1376(v w)	—	1325(v.w)	—
O-CH_3 Stretch	1222(v.w)	1238(m)	—	1225(v s)	1184(v w)	1231(v.s)
	-	1187(v.s)	—	1142(w)	—	1184(s)
	—	1140(v.s)	-	-	—	-
CH_3 rock	—	1058(v.s)	1037(m)	1030(w)	916(v s)	921(m)
	1023(w)	1036(v.s)	1013(v s)	1000(s)	1025(v w)	1023(s)
	—	924(m)	-	920(w)	—	—
δ(C-O-C)	383(w)	—	—	—	—	—
	332(w)	—	—	—	—	—

Green(1962) the assignments have been reversed in this paper. The two weak Raman lines at 383cm^{-1} and 332cm^{-1} are assigned as δ (C—O—C) for 1, 3, 5—trimethoxy benzene.

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